Confinement induces both higher free volume and lower molecular mobility in glycerol

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We report measurements of the local free volume and mobility of a glass-forming liquid (glycerol) confined in a mesoporous silica glass. The lower molecular mobility in confinement, measured by neutron scattering spectroscopy, is accompanied by a higher mean free volume size between molecules, measured by positron annihilation lifetime spectroscopy. The confined liquid appears to be perturbed to such an extent that the normally observed free volume/mobility relationship is reversed. This study shows that these effects originate locally at a molecular level. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2835903]

The glass transition of nanometer-sized materials has been of increasing interest to scientists since a landmark paper in 1991 reporting a decrease of glass transition temperature T_g for glasses formed in mesoporous media.[1] Subsequent studies have reported similar suppression of T_g for materials whose geometry is restricted both in 3 dimensions (e.g., in mesoporous glass)[2] and in 2 dimensions (part of thin films).[3] Other studies reporting the converse, an *increase* in T_g with restricted size,[4–6] indicate that both "pure" finite-size effects and surface effects play a role in determining T_g. "Pure" finite-size effects mean that the sample size approaches a length-scale associated with glass-forming phenomena, namely, the size of a cooperatively rearranging region.[7]

A deeper understanding of the physics of glass-forming fluids under confinement should contain relationships between structure and mobility. So far, connections of this sort are missing, despite many of the commonly used bulk glass transition theories elucidating precisely this (e.g., the theory of Cohen and Turnbull[8]). In this letter, we report observations that glycerol, a hydrogen-bonding liquid, has a lower mobility when confined in pores with strong surface-fluid interactions, but that the local free volume between molecules is higher than in bulk. This is a reversal of the relationship between these two parameters measured solely for bulk liquid.

Positron annihilation lifetime spectroscopy (PALS) is used to measure the size of low-electron density "holes" between molecules in soft condensed matter. The lifetimes [fitted using the program LT9 (Ref. 9)] are related via a semi-empirical equation[10,11] to the hole size,

$$\tau_{o\text{-Ps}} = 0.5\ \text{ns}\left[1 - \frac{r_h}{r_h + \delta r} + \frac{1}{2\pi}\sin\left(\frac{2\pi r_h}{r_h + \delta r}\right)\right]^{-1}. \quad (1)$$

$\tau_{o\text{-Ps}}$ is the (measured) ortho-positronium (o-Ps) lifetime, r_h is hole radius (potential well), and the Ps wavefunction overlaps with molecules within a layer δr of the potential wall. The spectrometer used is a fast-fast system[12] (resolution full width at half maximum =260 ps). The positron source was ^{22}Na prepared from aqueous ^{22}NaCl deposited between two pieces of 8 μm thick Kapton foil. The sample disks (≈2 mm thick filled with glycerol) were placed on either side of the source. The Vycor glass was cleaned prior to each experiment by boiling in 30% hydrogen peroxide, rinsing in deionized water, and then drying in a vacuum oven at 420 K. The pores have their native surface so the glycerol is strongly attracted to the surface via hydrogen bonding to the silica surface silanols. We do not observe a separate o-Ps lifetime from annihilation in the Vycor matrix. If one were present we would either resolve an extra lifetime component, or the χ^2

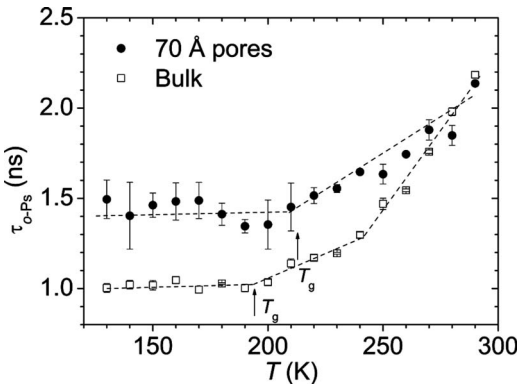

FIG. 1. Mean o-Ps lifetime for glycerol in bulk and confinement. Glass transition temperatures T_g are indicated from least squares fits of straight lines above and below the T_g region. Lines drawn are to guide the eye. For a discussion of possible origins of the increase in gradient at ≈240 K, see Bartoš *et al.* (Ref. 20). Error bars in all figures are ± one standard deviation.

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TABLE I. Glass transition temperatures of glycerol confined in silica glass.

Reference	6	15	16	This work
Glass	SBA15	Vycor	Sol-gel	Vycor
Technique	DSC	Solvation dynamics	DSC	PALS
Poresize, d (nm)	Glass transition temperature, T_g (K)			
3.6			189.9	
4		192		
5.6	193.6			
6.2			191.1	
7				211 (±4)
8.4	193.2			
11.8	191.4			
15.2			191.6	
26.4	191.6			
∞	189	188	188	198 (±3)

of the fit would improve as the glycerol lifetime approached that of the nonrelaxing matrix, neither of which happens.

Figure 1 shows the mean lifetime of *o*-Ps in bulk glycerol and glycerol confined to Vycor pores with mean diameter of 70 Å (pore diameters measured by nitrogen adsorption isotherms). The data for bulk glycerol are very similar to those reported previously.[13,14] From Fig. 1, (1) T_g is higher for confined glycerol (211 ± 4 K) than for bulk (198 ± 3 K); (2) $\tau_{o\text{-Ps}}$ is larger (at constant T) in confinement than in the bulk. Observation (1) must be considered alongside previous T_g measurements of glycerol in porous silica glasses where contradictory differences from bulk have been reported,[6,15,16] as shown in Table I, and also on other hydrogen-bonded liquids reporting higher T_gs when confined in silica glasses.[17] The higher T_g from PALS probably reflects differences already known to exist in determining values from different modes (and characteristic experiment times) of measurement, for example, that of 4 K between temperature modulated calorimetry and differential scanning calorimetry.[18] The increase with confinement observed by PALS is greater than that observed using other techniques. It has often been suggested that Ps probes regions of high free volume preferentially,[19] so this would mean that the regions of lower mobility and higher free volume coincide. The second apparent increase in the expansivity of $\tau_{o\text{-Ps}}$ at 242 ± 1 K has been observed before for bulk glycerol.[20]

Using Eq. (1) on the mean *o*-Ps lifetimes, observation (2) suggests a larger free volume hole size in confinement (46 ± 2 Å^3) than in bulk (20.3 ± 0.2 Å^3) (both below T_g). The lifetime spectrum for confined glycerol required a distribution of *o*-Ps lifetimes, $\sigma_{\tau,o\text{-Ps}}$, whereas bulk glycerol was adequately described by a discrete *o*-Ps lifetime. One can calculate a hole volume distribution from $\tau_{o\text{-Ps}}$ and $\sigma_{\tau,o\text{-Ps}}$ (Ref. 19) (1.40 and 0.45 ns for our data below T_g) and then take a numerical average of this to get a mean volume of 40 ± 2 Å^3.

These local free volume measurements are complemented by measurements of local mobility using neutron scattering spectroscopy. The High-Flux Backscattering Spectrometer[21] (resolution of ≈1 μeV→resolvable timescales of ≈2 ns, which is commensurate with the lifetimes measured by PALS) at the NIST Center for Neutron Research was used in elastic mode. The sample was sealed in an annular aluminum can on a closed-cycle refrigerator. The "confined" sample contained Vycor powder, confined glycerol, and bulk glycerol in the space between the powder granules; the ratio of confined to bulk glycerol being 20:80. The signal from confined glycerol is obtained by subtracting a bulk component from the total signal. Due to the large scattering cross section of hydrogen, Vycor contributes 1.8% of the total scattering intensity, which we assume to be negligible for our calculations. The two sample setups contain different amounts of glycerol and, therefore, exhibit different levels of multiple scattering (MS). As noted by Wuttke,[22] increased MS leads to an underestimation of the mean-squared displacement ($\langle u^2 \rangle$) of scatterers in the sample, which is the quantity commonly used to quantify mobility in such experiments. We account for MS in the analysis by fitting the data to the equation suggested by Zorn,[23]

$$\ln\left[\frac{\tilde{I}_{\text{el}}(Q)}{\tilde{I}^0_{\text{el}}(Q)}\right] = \ln\left\{(1-s)\left[I_{\text{el}}(Q) + \frac{s\bar{I}^2_{\text{el}}}{1-s\bar{I}_{\text{el}}}\right]\right\}, \qquad (2)$$

where $\tilde{I}_{\text{el}}$ is the measured intensity at scattering vector Q, "0" denotes the low-temperature intensity (at 5 K); I_{el} is the intensity without MS; s parametrizes the MS; and $\bar{I}_{\text{el}}$ is the solid-angle average of the elastic (single) scattering. We follow the common procedure in assuming a normalized Gaussian self-correlation function for the scattering particles so $I_{\text{el}} = \exp(-\langle u^2 \rangle Q^2/3)$ and $\bar{I}_{\text{el}}$ follows from this. The Gaussian form is only applicable for nondiffusive motion, so we restrict fitting to the temperature range below 250 K where no quasielastic broadening of the elastic peak is seen.

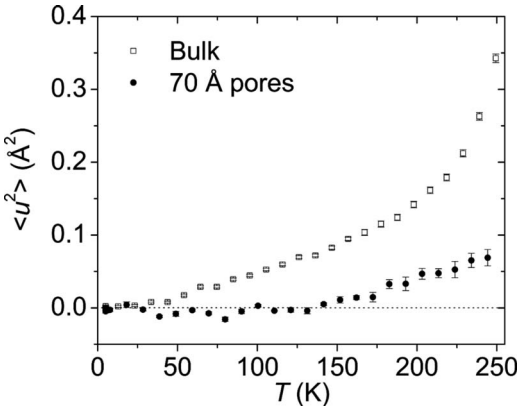

FIG. 2. Mean squared displacements $\langle u^2(T) \rangle$ for glycerol in bulk and confinement. Values derived from elastic scattering scans using the High-Flux Backscattering Spectrometer at NIST at $Q = 0.25$ to 1.75 Å^{-1}.

Figure 2 shows $\langle u^2 \rangle$ vs. T for bulk and confined glycerol. In the region around 200 K $\langle u^2 \rangle$ starts to rise more quickly. This is most likely to be due to the onset of nonharmonic motion in glass-forming materials. The higher $\langle u^2 \rangle$ in bulk is consistent with a higher molecular mobility responsible for the lower T_g in bulk. Soles *et al.* reported a similar reduction in $\langle u^2 \rangle$ for polymeric thin-film glass formers.[24] The $\langle u^2 \rangle$ values here are significantly larger than those reported in the literature for glycerol[25,26] which were calculated using the Q range from 3 to 5 Å^{-1} and energy resolution of 4.5 μeV, whereas those reported here were from $Q = 0.25$ to 1.75 Å^{-1}. $\langle u^2 \rangle$ is not directly a measure of diffusive motion. Formally, it represents local motion not structural relaxation, but is still supposed to be keenly influenced by free volume; a previous

study with PALS supported this view.[27] For a thorough discussion on interpreting $\langle u^2 \rangle$ with relation to T_g, particularly for confined media, see Ref. 24. The lower $\langle u^2 \rangle$ in confinement is in contradiction with conventional free-volume models of molecular mobility in glass-forming materials (high mobility=high free volume). These results are surprising and seem to contradict assumptions made previously that higher T_gs in confinement result, in part, from lower free volume.[4,17]

A distribution of *o*-Ps lifetimes in glycerol in confinement and no observable distribution in bulk suggests a free volume structure which varies with position in a pore. It is likely that this results from an interfacial layer of glycerol close to the pore walls. Previous dynamic studies have reported a "sluggish," or even immobile, layer of hydrogen-bonding molecules at the surface of nanopores, calculated to be 9 Å for 25 Å (diameter) pores.[17,28] Further evidence of increased heterogeneity for confined glycerol comes from a smaller stretching KWW β exponent, indicating a larger dispersion of relaxation times.[15] From our results it is not explicit whether this layer has higher or lower free volume than the glycerol in the center of the pore, only that the free volume overall in the pore is greater than in bulk and that it is not uniformly distributed. As mentioned earlier, however, Ps preferentially probes areas of high free volume and the T_g difference between bulk and confined from PALS is greater than for other measurements; this might indicate higher free volume in the surface, less mobile, layer.

Previous studies on macroscopic properties of toluene[29] and benzene[30] reported a lower density of fluids in confinement, together with decreased molecular mobility as reflected, for example, in a higher T_g. Our results measure a higher *local* free volume together with a lower *local* molecular mobility for a confined glass former. This suggests a reversal of the conventional free volume rules for molecular mobility. With respect to this conclusion, the fact that glycerol is a strongly hydrogen-bonded liquid is important. The additional constraints placed upon the motion of molecules by the walls are strongly transmitted to nonsurface layers due to their hydrogen-bonded network. This may be the reason that the structure does not relax as much as it would in bulk, resulting in the more open structure alongside lower mobility. It is hoped that further study on such systems will prove useful in the on-going effort to understand the bulk glass transition.

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